

Experimental and theoretical study of nanofiltration of weak electrolytes: $\text{HSO}_4^-/\text{SO}_4^{2-}$ system

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Introduction

Over recent years, nanofiltration (NF) has been considered as an effective way to improve processing steps in metallurgical and hydrometallurgy applications dealing with mixtures of metal ions in sulphuric-acid-dominated solutions. The principal advantage of NF membranes is the ability to allow a practically free passage of acid, while metallic species are efficiently rejected, especially multi-charged species (Mullet et al., 2013). In general, these sulphuric solutions cover a range from strongly acidic solutions with pH below 1 up to moderately acidic solutions of pH 3. Over this range, changes in the feed acidity influence both the aqueous electrolyte solution speciation ($\text{SO}_4^{2-}/\text{HSO}_4^-/\text{H}^+$) and the membrane acid-base properties.

In this study, experimental data on the sulphuric-acid rejection, for pH values from 1 to 3, have been obtained with an aromatic poly(piperazine)amide membrane (NF270) at various trans-membrane pressures. The results were modelled by a novel version of Solution-Electro-Diffusion model taking into account equilibrium reactions and a general (quasi)analytical solution was obtained for the transport of weak electrolytes of arbitrary valence type. From the modelling procedure, permeances to H^+ , HSO_4^- and SO_4^{2-} over the studied pH range were determined.

Material and Methods

Experiments were performed with NF270 membrane in a cross-flow set-up equipped with a test cell (GE SEPA™ CF II). Aqueous solutions of H_2SO_4 were used as feed solutions with pH values between 1 and 3. By this way, it was studied the range where HSO_4^- was the dominant species (below the pKa of the $\text{HSO}_4^-/\text{SO}_4^{2-}$ equilibrium) and the range where SO_4^{2-} was dominant (above the pKa).

The ion fluxes were described according to the Solution-Electro-Diffusion model. Ion transport was subjected to zero-current and electro-neutrality condition. Virtual ion concentrations are not independent but related by a chemical equilibrium condition at a given constant temperature and ionic strength.

Results and Discussion

Figure 1 shows the rejection of total sulphate species ($\text{SO}_4^{2-}/\text{HSO}_4^-$). It increased quasi-linearly for all the experiments (apart from pH 3 and pH 2.7) up to values

between 30 to 35% at the maximum achieved trans-membrane volume flow (40-50 $\mu\text{m/s}$), without reaching the typical values obtained with sulphate solutions at neutral to basic conditions (>99%) in the same trans-membrane volume flows (Pagès et al, 2017). At pH 3, the total sulphate rejection reaches values around 75 %, which is still reduced compared with sulphate rejections at neutral pH due to the presence of HSO_4^- species in the feed. When pH was lowered the amount of HSO_4^- species increased significantly, leading to lower sulphate rejections (around 35%). NF270 has an isoelectric point (IEP) around 3 (Mullet et al., 2013) which makes membrane positively charged when pH is below IEP. In all our experiments the pH was lower than IEP, making the membrane charge positive and increasing when pH was lowered. However, the low total sulphate rejection could also be primarily related to the low degree of dissociation of the acid. As pH decreases, the total amount of HSO_4^- increases and it becomes dominant in solution. This change of feed composition resulted in a lower rejection of total sulphate. Membrane permeances showed higher values for HSO_4^- than for SO_4^{2-} , in agreement with dielectric exclusion mechanism. High values were obtained for H^+ that could be described by its high mobility.

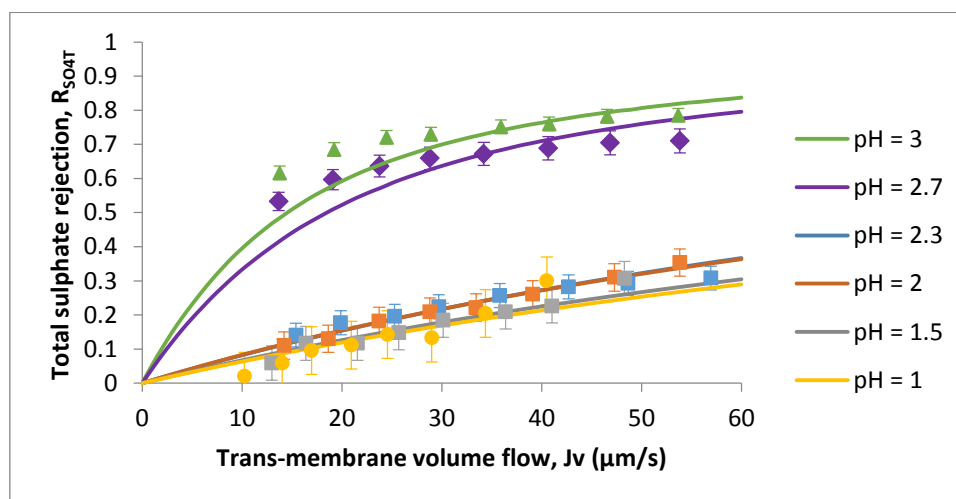


Figure 1. Total sulphate ($\text{SO}_4^{2-}/\text{HSO}_4^-$) rejection in solutions at different pH values as a function of trans-membrane volume flow. Solid lines were obtained by the Solution-Electro-Diffusion model.

Conclusions

Our experimental study of transport of sulphuric solutions within a pH range covering the ratios between SO_4^{2-} and HSO_4^- species from 1/10 to 10/1 reveals strong influence of the speciation on electrolyte rejection. The principal reason for this is the strong dependence of ion permeance of NF membranes on the magnitude of ion charge (probably due to dielectric exclusion). The experimental data could be quantitatively interpreted by means of Solution-Electro-Diffusion model extended to account for an equilibrium chemical reaction between the species.

References

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